

Table 2. Selected interatomic distances (Å) and angles (°) with *e.s.d.*'s in parentheses

| | | | |
|---------------------------------|------------|----------------|------------|
| Framework, model I* | | | |
| Si—O1 | 1.6167 (9) | Al—O1 | 1.7383 (9) |
| O1—Si—O1 (2 ×) | 113.2 (1) | O1—Al—O1 (2 ×) | 111.3 (1) |
| O1—Si—O1 (4 ×) | 107.6 (1) | O1—Al—O1 (4 ×) | 108.6 (1) |
| Si—O1—Al | 140.2 (1) | | |
| Na coordination, model I | | | |
| Na···O1 | 2.353 (2) | Na···O1 | 3.043 (2) |
| Na···O2 | 2.47 (5) | Na···O2 | 2.54 (5) |
| Na···O2 | 3.16 (3) | Na···N | 2.48 (1) |
| Na···N | 3.01 (1) | | |
| Na coordination, model II | | | |
| Na···O1 | 2.353 (2) | Na···O1 | 3.043 (2) |
| Na···O2 | 2.47 (5) | Na···O2 | 2.54 (5) |
| Na···O2 | 3.14 (3) | Na···N | 2.67 (1) |
| Na···N | 3.09 (2) | | |
| NO ₂ anion, model I | | | |
| N—O2 (2 ×) | 1.18 (3) | O2—N—O2 | 104 (2) |
| O2···O1 | 3.54 (3) | N···O1 | 4.03 (1) |
| NO ₂ anion, model II | | | |
| N—O2 (2 ×) | 1.25 (3) | O2—N—O2 | 109 (5) |
| or | | | |
| N—O2 (2 ×) | 1.27 (3) | O2—N—O2 | 104 (5) |
| O2···O1 | 3.54 (3) | N···O1 | 4.03 (3) |

* For model II no significant differences.

Strong Na···N interactions, which clearly exist in the structure, have not been found in the earlier structure analyses. These interactions are also required from valence bond considerations. The Na environments discussed recently (Kempa *et al.*, 1990) with one cation being fivefold, two cations being fourfold, and one cation being threefold bonded to O2 and/or O1 atoms are very unlikely, because of the highly inhomogeneous coordinations and unbalanced valences. These are, and can obviously only be,

avoided with the N atom in off-centre position. No strong interactions occur between atoms of the anion and O1 framework atoms: N···O1 ≥ 4.03 (1) Å, and O2···O1 ≥ 3.54 (4) Å.

At room temperature the orientational disorder has to be regarded as dynamic in nature, at least on the NMR time scale. This is shown by the single quadrupolar ²³Na MAS NMR signal, which reveals that on average in time only one kind of Na coordination exists in the structure (Kempa *et al.*, 1990).

We are grateful to Dr G. Engelhardt for performing NMR measurements.

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Acta Cryst. (1991). **C47**, 501–503

Structure of K₃Na[Re₂O₃(CN)₈].2H₂O

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(Received 22 June 1990; accepted 20 August 1990)

Abstract. Potassium sodium μ -oxo-bis[oxotetra-cyanorhenium(V)] dihydrate, $M_r = 804.9$, ortho-

rhombic, $Fmmm$, $a = 8.207$ (2), $b = 13.715$ (5), $c = 16.199$ (7) Å, $V = 1823$ (1) Å³, $Z = 4$, $D_x = 2.932$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 14.2$ mm⁻¹, $F(000) = 1464$, $T = 295 \pm 1$ K, $R = 0.035$

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for 658 observed reflections. The coordination sphere around the Re atom is a distorted octahedron with four cyano ligands forming the basal plane and two O atoms occupying the apical positions. One of these connects the two oxotetracyanorhenium(V) units to form a dimer. The μ -oxo-bis[oxotetracyanorhenium(V)] ions form columns in the *b* direction. The rhenium complexes are to some extent connected by hydrogen bond formation *via* the water molecules, but the structure is held together mainly by van der Waals forces.

Introduction. Different oxocyanorhenate complexes and their physicochemical properties have been the object of several considerations during recent years (Howard-Lock, Lock & Turner, 1982; Nadziejka & Stasicka, 1974, and the literature cited therein). Among those studies the crystal structures of two complexes have been determined and discussed, namely those of K₃[ReO₂(CN)₄] (Fenn, Graham & Johnson, 1971; Murmann & Schlemper, 1971) and [Pt(NH₃)₄]₂[Re₂O₃(CN)₈] (Shandles, Schlemper & Murmann, 1971). For comparison we have now determined the crystal structure of the earlier prepared complex K₃Na[Re₂O₃(CN)₈].2H₂O (Nadziejka & Stasicka, 1974) and the results are reported in this paper.

Experimental. The title compound was prepared as described earlier (Nadziejka & Stasicka, 1974). X-ray measurements were made on well developed prismatic violet crystals, 0.1 × 0.2 × 0.2 mm, separated after 6–10 days in the mother liquor, an aqueous methanol–acetic acid solution. Intensity data were measured at 295 ± 1 K with a Nicolet P3F diffractometer using graphite-monochromated Mo K α radiation and $\omega/2\theta$ scan: 5 ≤ 2 θ ≤ 58°. The lattice parameters were determined from 11 reflections (2 θ range 10–21°). The intensity data were corrected for Lorentz and polarization effects and for absorption through the φ -scan technique with maximum transmission factor = 1.000 and minimum = 0.336. Corrections for extinction were considered unnecessary. 699 unique reflections, 658 with $I \geq 3\sigma(I)$ were measured with $h 0 \rightarrow 11$, $k 0 \rightarrow 18$, $l 0 \rightarrow 22$; scan speed 2.0–29.3° min⁻¹. Two standard reflections (042, 131) showed no significant intensity variations. The structure was solved by Patterson and Fourier methods. The H atoms were not located. A full-matrix anisotropic refinement of 44 parameters yielded $R = 0.035$, $wR = 0.040$; $w = 1/[\sigma^2(F_o) + 0.005046F_o^2]$; max. $\Delta/\sigma = 0.008$, min. $\Delta/\sigma = -0.008$ in final cycle. The final $\Delta\rho$ map showed max. and min. heights 2.55 and -4.19 e Å⁻³ near the Re atom. The scattering factors and corrections for anomalous dispersion were from *International Tables for X-ray Crystallography* (1974, Vol. IV). The calculations were performed

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^4$) (Hamilton, 1959) for non-H atoms with *e.s.d.*'s in parentheses

$$U_{\text{eq}} = (U_{11} + U_{22} + U_{33})/3.$$

| | <i>x</i> | <i>y</i> | <i>z</i> | U_{eq} |
|------|-----------|------------|----------|-----------------|
| Re | 0 | 3590.1 (3) | 0 | 135 (3) |
| K(1) | 5000 | 5000 | 0 | 560 (46) |
| K(2) | 5000 | 0 | 2489 (3) | 365 (21) |
| Na* | 0 | 2500 | 2500 | 429 (93) |
| O(1) | 0 | 5000 | 0 | 288 (92) |
| O(2) | 0 | 2327 (8) | 0 | 176 (50) |
| O(3) | 2500 | 2500 | 2500 | 303 (56) |
| N(1) | 2775 (11) | 3856 (5) | 1416 (6) | 353 (38) |
| C(1) | 1815 (10) | 3728 (5) | 923 (5) | 211 (32) |

* Population parameter 0.5.

Table 2. Selected interatomic distances (\AA) and angles ($^\circ$)

| | | | |
|------------------------|------------|-----------------------------|-----------|
| Re—O(1) | 1.934 (1) | C(1)⋯C(1 ⁱⁱⁱ) | 2.98 (1) |
| Re—O(2) | 1.732 (11) | N(1)⋯N(1') | 3.14 (1) |
| Re—C(1) | 2.119 (8) | N(1)⋯K(1) | 3.325 (9) |
| O(3)—Na | 2.052 (1) | | |
| C(1)—N(1) | 1.136 (12) | N(1)⋯K(2 ^{iv}) | 2.99 (1) |
| Re⋯Re ^(c) | 3.867 (2) | N(1)⋯Na | 3.425 (9) |
| Re⋯K(1) | 4.536 (1) | N(1)⋯Na ^(c) | 3.142 (9) |
| Re⋯K(2 ^{iv}) | 4.472 (5) | O(2)⋯K(1 ^v) | 3.19 (1) |
| Re⋯Na | 4.317 (3) | O(3)⋯N(1) | 2.568 (8) |
| K(1)⋯K(2) | 4.067 (5) | | |
| K(1)⋯C(1) | 3.480 (8) | | |
| O(1)—Re—C(1) | 84.9 (2) | C(1)—Re—C(1 ⁱⁱ) | 89.3 (4) |
| O(2)—Re—C(1) | 95.1 (2) | Re—C(1)—N(1) | 176.3 (7) |
| O(1)—Re—O(2) | 180.0 (4) | | |

Symmetry code: (i) $x, 1 - y, z$; (ii) $x - 0.5, y + 0.5, z$; (iii) $1 - x, y, z$; (iv) $x, y + 0.5, 0.5 - z$; (v) $x + 0.5, y, z$; (vi) $x - 0.5, y - 0.5, z$.

with *SHELX76* (Sheldrick, 1976), *SHELXS86* (Sheldrick, 1986) and *XTAL* (Hall & Stewart, 1989) on a VAX 8650 computer.

Discussion. The atomic coordinates for K₃Na[Re₂O₃(CN)₈].2H₂O are given in Table 1* and selected interatomic distances and angles in Table 2. Fig. 1 illustrates the geometry and the atom labeling of the compound. The crystal packing is shown in Fig. 2.

The crystal structure is composed of K⁺, Na⁺ and Re₂O₃(CN)₈⁴⁻ ions beside H₂O molecules (Figs. 1 and 2). The structure is held together by hydrogen bonding and van der Waals forces. In the binuclear Re anion the coordination geometry about the Re atom is a distorted octahedron with four cyano ligands occupying the basal plane positions and two O atoms the apical positions. The anion has a linear

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53500 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

OReOReO arrangement (180.0°). The largest deviation from 90° of the C—Re—O angles is 5.1° . The terminal Re—O distance of $1.732(11)$ Å is considerably shorter than that of the bridged oxygen, $1.934(1)$ Å (Fig. 1 and Table 2). These values can be compared with the corresponding distances $1.698(7)$ and $1.915(1)$ Å, respectively, in $[\text{Pt}(\text{NH}_3)_4]_2[\text{Re}_2\text{O}_3(\text{CN})_8]$ (Shandles, Schlemper & Murmann, 1971). The C—Re—C angle differs from those of the mentioned complex within $1-2^\circ$. For comparison, the structure of the monomer $\text{K}_3[\text{ReO}_2(\text{CN})_4]$ gives an Re—O distance of $1.781(3)$ Å, assumed to be a double bond (Murmman & Schlemper, 1971). On the basis of these values it may be concluded that the bridging Re—O(1) bond is nearest to a single-bond length and the terminal Re—O(2) bond has some triple-bond character (Fenn, Graham & Johnson, 1971).

The cyano groups on the Re atoms are carbon bonded in the normal way as in most stable metal complexes. The Re—C distance $2.119(8)$ Å is identi-

cal to the $2.124(7)$ and $2.115(7)$ Å found in $[\text{Pt}(\text{NH}_3)_4]_2[\text{Re}_2\text{O}_3(\text{CN})_8]$ but about $0.01-0.02$ Å shorter than in $\text{K}_3[\text{ReO}_2(\text{CN})_4]$ [$2.130(3)$ and $2.139(3)$ Å]. The C—N bond distance of $1.136(12)$ Å is quite typical and appears to be similar to the distances $1.130(9)$ and $1.137(9)$ Å found in $[\text{Pt}(\text{NH}_3)_4]_2[\text{Re}_2\text{O}_3(\text{CN})_8]$ but somewhat shorter than the distances $1.154(5)$ and $1.156(5)$ Å in $\text{K}_3[\text{ReO}_2(\text{CN})_4]$. The deviation from 180° of the Re—C—N angle is due either to packing considerations or to interaction with the potassium ions (Table 2).

The cyano ions of the complex are perfectly eclipsed. This may imply appreciable π bonding in the bridge Re—O—Re because the distance $\text{N}(1)\cdots\text{N}(1')$ is $3.14(1)$ Å.

The $\text{O}(3)\cdots\text{N}(1)$ contact of $2.568(8)$ Å indicates very strong hydrogen bonding. Such interaction would, however, be expected to cause only minor deviations in the bond angles and distances in the rhenium complex ions. All other interatomic distances are significantly longer than van der Waals contacts.

The thermal parameters* may be seriously affected by the high non-uniform absorption which is almost certainly not completely accounted for by the absorption corrections. On this basis it may be concluded that the alkaline metal ions would be thermally most labile and the water molecules and cyano groups about equally labile in the crystal structure.

The present results together with those for $[\text{Pt}(\text{NH}_3)_4]_2[\text{Re}_2\text{O}_3(\text{CN})_8]$, form structural evidence for the binuclear $\text{Re}_2\text{O}_3(\text{CN})_8^{4-}$ ion.

* See deposition footnote.

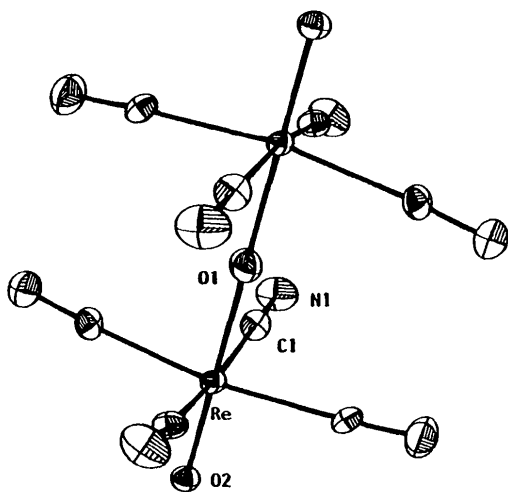


Fig. 1. ORTEP (Johnson, 1965) drawing with the numbering scheme of the $[\text{Re}_2\text{O}_3(\text{CN})_8]^{4-}$ ion.

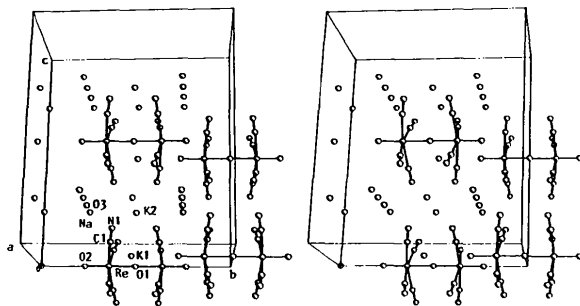


Fig. 2. PLUTO (Motherwell & Clegg, 1978) stereoview of the molecular packing.

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